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ORIGINAL ARTICLE

Chemical composition analysis of the essential oil of *Solanumn nigrum* L. by HS/SPME method and calculation of the biochemical coefficients of the components

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Abstract The volatile constituents of the essential oil of wild *Solanumn nigrum* L. obtained from the Kurdistan of Iraq were extracted by head-space/solid-phase micro-extraction (HS/SPME) and were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Of a total of twenty compounds in the oil, all of them were identified. The main components were as follows: Dillapiole (22.22%), α-Cadinol (16.47%), *para*-Cymene (10.01%), (E)-1-(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one or *β*-damascenone (9.08%), α-Phellandrene (8.48%), *β*-Pinene (5.93%), α-Bisabolol acetate (4.53%), (Z,E)-4,6,8-Megastigmatriene (4.09%), Phytol (2.49%), Linalyl butanoate (2.13%), 8-methylene-tricyclo[3.2.1.0(2,4)]octane (2.60%) and Limonene (2.03%). Some physicochemical properties, such as the logarithm of calculated octanol–water partitioning coefficients ($log\,K_{ow}$) and total biodegradation (TB_d in mol/h) were calculated for compounds **1**–**20** from *S. nigrum* L.

1. Introduction

The *Solanum nigrum* complex also known as *Solanum* L. section *Solanum*, is a group of the *Solanum* species (Edmonds and Chewya, 1997; Zargari, 1991). Sometimes *S. nigrum* is confused for deadly nightshade, a different Solanaceae species altogether (Edmonds and Chewya, 1997; Zargari, 1991). Other names of *S. nigrum* are European Black Nightshade or locally

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just black nightshade, Duscle, Garden Nightshade, Hound's Berry, Petty Morel, Wonder Berry, Small-fruited black nightshade. It is a species of the *Solanum* genus, native to Eurasia and introduced in the Americas, Australia, Asia and South Africa. Parts of this plant can be highly toxic to livestock and humans, and it is considered a weed. Nonetheless, ripe berries and cooked leaves are used as food in some locales; and plant parts are used as a traditional medicine (Edmonds and Chewya, 1997; Zargari, 1991; Mohy-ud-dint et al., 2010). The plant has a long history of medicinal usage, dating back to ancient Greece (Edmonds and Chewya, 1997; Grieve, 1984). It was a traditional European medicine used as a strong sudorific, analgesic and sedative with powerful narcotic properties. Some strong toxicities of this type of herb were reported (Grieve, 1984; Schauenberg and Paris, 1997). *S. nigrum* L. is an important ingredient in traditional medicine (Jain, 1968). The juice of the plant is used on ulcers and other skin diseases (Jain, 1968). Traditionally the plant was used to cure tuberculosis (Kaushik et al., 2009). This plant's leaves are used to treat mouth ulcers (Edmonds and Chewya, 1997). *S. nigrum* is a widely used plant in oriental medicine. It is anti-tumor gene agent, antioxidant, anti-inflammatory, hepato-protective, diuretic and antipyretic (Jain et al., 2011). The experiments of Chinese medicine confirm that this herb inhibits growth of cervical carcinoma (Jian et al., 2008). In 2008, Jian et. al., have reported that the aqueous extract of *S. nigrum* inhibits growth of cervical carcinoma (U14) via modulating immune response of tumor bearing mice and inducing apoptosis of tumor cells (Jian et al., 2008).

Some of the parameters like $\log K_{ow}$ and TB_d were calculated for compounds **1**–**20** of this herb. The parameter of $\log K_{ow}$ is used in many environmental studies to help determine the environmental fate of chemicals (Hansh et al., 1995; Bundy et al., 2001; Li and Yalkowsky, 1998). The biodegradation studies show that microbial biosensors are a viable alternative means of reporting on potential biotransformation (Degner et al., 1991; Cronin and Dearden, 1995).

The *S. nigrum* L. sample used in this study was collected from the Sulaimani Kurdistan (around Sulaimani, Kurdistan, Iraq). A voucher specimen has been deposited in the Herbarium of the Research Center of Agriculture and Natural Resources, Sanandaj-Kurdistan, Iran. The local name of *S. nigrum* L. in Kurdistan is *Giya Mara* (*GIYA-MARA*). The *S. nigrum* L. was utilized as a medicinal herb in local and traditional medicine (in Kurdistan). The aerial parts of this herb in crude or baked form were utilized as an active agent especially for the snaked persons. There is no official publication about the mentioned effects of *S. nigrum* L. but just reports by the local folks. Also, it is very sensitive toward decreasing the amount of cholesterol of blood. Some unpublished reports in Kurdistan showed the decreasing of the blood sugar after using this *S. nigrum* L.

2. Analytical methods

Solid-phase micro-extraction (SPME) is a sampling technique based on the absorption of analysts on or into a polymeric material that coats a silica fiber. SPME fits into a trend of developing analytical techniques for small sample volumes, reduced solvent consumption, and shorter analysis time, while maintaining or improving sensitivity. Recent advances in the development of analytical methods based on headspace/solid-phase micro-extraction (HS/SPME) of natural aroma compounds have been reviewed, with a special emphasis on increasing reproducibility (Stashenko and Martínez, 2007; Barié et al., 2006; Cimato et al., 2006; Johnson et al., 2004). A simple, rapid, efficient and inexpensive method for the determination of essential oil in different samples is headspace-solid phase micro-extraction/gas chromatography-mass spectrometry (HS/SPME–GC/MS). The present method has provided good reproducibility and recovery. HS/SPME–GC/MS has been used to determine the essential oils in analytical samples and may be a potential tool for the quality assessment of medicinal herbs like *S. nigrum* L. (Stashenko and Martínez, 2007; Barié et al., 2006; Cimato et al., 2006; Johnson et al., 2004). The HS/SPME–GC/MS method offers high resolution chemical maps of different samples without thermal effects.

3. Materials and methods

Dried aerial parts of *S. nigrum* L. were subjected to the SH/SPME method (headspace/solid-phase micro-extraction) for 15 min, 70 °C equilibrium temperature and SPME fiber (polydimethylsiloxane (PDMS) 100 μm, red) to produce a yellow oil in 0.28% (w/w) yield. The essential oil of the aerial parts of *S. nigrum* L. was examined by GC/MS (GC: HP 6890, MS: HP 5973) using a HP5-MS column (30 m 0.25 mm fused silica capillary column, film thickness 0.32 μm). The temperature program ranged from 60 °C (3 min) −210 °C (2 min) with an increase rate of 6 °C/min (injection temperature 250 °C, carrier gas: helium (with purity 99.999%). The detector temperature was at 150 °C, the ionization energy in mass was 70 eV, the mass range was 10–300 amu, and the scan time was 1 s.

The list of identified components is presented in Table 1. The constituents were identified by comparing their MS spectra with those in a computer library or with authentic compounds. The identifications were confirmed by comparing their retention indices with those of authentic compounds or with data in the literature (Adams, 1995; Parker, 1974; Hawley, 1997; Hocking, 1992). In the aerial parts of wild *S. nigrum* L., the identified components and the relative amounts based on peak area were: Dillapiole (22.22%), α-Cadinol (16.47%), *para*-Cymene (10.01%), (E)-1-(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one or β-damascenone (9.08%), α-Phellandrene (8.48%), β-Pinene (5.93%), α-Bisabolol acetate (4.53%), (Z,E)-4,6,8-Megastigmatriene (4.09%), 8-methylenetricyclo[3.2.1.0(2,4)]octane (2.60%), Phytol (2.49%), Linalyl butanoate (2.13%), and Limonene (2.03%). The calculated data of the octanol–water partitioning coefficients ($\log K_{ow}$) and the total biodegradation TB_d (mol/h) were calculated by EPI-suit v4.00 package (EPI-suit v4.00) see Table 1.

4. Results and discussion

The extraction and nutritional properties of *S. nigrum* L. seed oil were investigated before (Dhellot et al., 2006). *S. nigrum* L. is an annual herbaceous plant. It is a rather common species in wet woods, near rivers and old walls. In India this is herb mixed with other herbal medicines. This herb had shown a hepato-protective effect in cirrhotic patients. This

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Table 1 Essential oil constituents (percentages and Kovats indices (KI)), logarithm of calculated octanol–water partitioning coefficients ($log\,K_{ow}$) and total biodegradation (TB_d in mol/h) of *Solanumn nigrum* L.

Total biodegradation (TB_d; mol/h × 10^{-5})	$log\,K_{ow}$[b]	KI[a]	%	Compounds	No.
0.81	4.27 (4.44)[c]	975	5.93	β-Pinene	**1**
0.11	4.91 (4.65)	1034	1.05	1(7)-p-Menthene	**2**
0.04	4.83 (4.55)	1041	2.03	Limonene	**3**
1.05	4.35 (4.16)	1123	0.93	α-Pinene	**4**
5.30	3.31 (3.25)	1180	1.33	2-Methylisoborneol	**5**
9.00	4.62 (4.41)	1194	8.48	α-Phellandrene	**6**
0.10	4.00 (4.01)	1215	10.01	*para*-Cymene	**7**
0.12	5.97	1386	4.09	(*Z,E*)-4,6,8-Megastigmatriene	**8**
0.28	5.00 (4.77)	1577	0.39	Lauric acid	**9**
4.50	3.71	1612	2.60	8-Methylene-tricyclo[3.2.1.0(2,4)]octane	**10**
29.00	4.86	1627	1.92	γ-Eudesmol	**11**
21.00	4.32 (4.90)	1652	16.47	α-Cadinol	**12**
28.00	5.37 (4.93)	1766	2.13	Linalyl butanoate	**13**
29.00	6.63 (5.68)	1792	4.53	α-Bisabolol acetate	**14**
9.30	3.61	1829	22.22	Dillapiole	**15**
0.21	4.21 (3.10)	1848	9.08	(E)-1-(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one (β-damascenone)[d]	**16**
23.00	7.07	1863	1.89	Laurenene	**17**
29.00	4.89	1879	1.67	5-Epi-Paradisol	**18**
34.00	5.98 (5.79)	1771	0.75	Myristic acid	**19**
26.00	8.32 (8.23)	2116	2.49	Phytol	**20**

[a] Kovats index.
[b] The values were calculated by EPI-suit v4.00 package.
[c] The values in parentheses are the experimental values for logarithm of octanol–water partitioning coefficients ($log\,K_{ow}$). (http://www.chemspider.com/).
[d] For KI, see reference (Klesk et al., 2004).

protective effect can be attributed to the anti-inflammatory, diuretic and anti-oxidative properties of the component herbs (Dhellot et al., 2006; Fallah Huseini et al., 2005). This herb also protects against hepatitis B virus infection B (Dhellot et al., 2006; De Silva et al., 2003; Galitskii et al., 1997; Kalab and Krechler, 1997). It has been reported that the extract of its fruits has anti-tumor and neuro-pharmacological properties. *S. nigrum* L. can be used as an anti-oxidant and cancer chemo-preventive matter (Dhellot et al., 2006; Son et al., 2003; Perez et al., 1998). This herb is known for its toxic effects because it contains solanine, a neurotoxic glyco alkaloid (Abbas et al., 1998).

Table 1 shows Dillapiole (22.22%) **16**, α-Cadinol (16.47%) **12** and *para*-Cymene (10.01%) **6** have the highest percentage amongst the twenty-two components that were identified. (E)-1-(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one or β-damascenone (9.08%) **9**, α-Phellandrene (8.48%) **5**, β-Pinene (5.93%) **1**, α-Bisabolol acetate (4.53%) **15**, (Z,E)-4,6,8-Megastigmatriene (4.09%) **8**, 8-methylene-tricyclo[3.2.1.0(2,4)]octane (2.60%) **10**, Phytol (2.49%) **20**, Linalyl butanoate (2.13%) **14**, and Limonene (2.03%) **7** are located in the second level of the concentration in the essential oil of this herb. The data in Table 1 show, components **11**, **17**, **18**, **4**, **2**, **3**, **14**, **19** and **13** have the relative percentages, respectively. The biological effects of the main compounds are discussable in terms of their possible use in medicine and foods (Hawley, 1997; Hocking, 1992). Table 1 shows that phytol (2.49%) **20** has the highest amount of $log\,K_{ow}$, among **1**–**20**. Meanwhile, 2-Methylisoborneol (1.33%) **4** has the lowest amount of $log\,K_{ow}$. The calculations show that the **19** and **6** have the highest and lowest amounts of TB_d, respectively.

5. Conclusion

Twenty components in the essential oil of *S. nigrum* L., which were collected from Soleimania–Kurdistan area in Iraq, were extracted by the HS/SPME method and they identified by GC/MS. Dillapiole, α-Cadinol and *para*-Cymene were the most abundant of the essential oils identified. The parameters of $log\,K_{ow}$ and TB_d were calculated for the components **1**–**20**.

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